

# Crystal-field splittings in CeX (X= N, P, As, Sb, Bi) compounds

P. Roura-Bas <sup>a,\*</sup>, V. Vildosola <sup>a,b</sup> and A. M. Llois <sup>a,b</sup>

<sup>a</sup> *Departamento de Física, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica*

<sup>b</sup> *Departamento de Física, Universidad de Buenos Aires, Buenos Aires, Argentina*

The unusual and interesting physical properties of rare earth intermetallic compounds have their origin in the combination of strongly correlated 4f states and their hybridization with the conduction electron sea, which gives rise to their complex low temperature Kondo behavior. In particular, Ce compounds are very sensitive to the crystalline and chemical environment, as compared to other rare earth systems. The interaction of the 4f state with the conduction band plays an important role in the determination of the different magnetic, structural and transport properties of these systems. Among the cerium compounds, those of the type CeX, which crystallize in the rock salt structure, exhibit extremely unusual magnetic properties. By making use of the mixed LDA-NCA calculation technique we analyse the crystal-field splittings of CeX compounds (X=N, P, As, Sb, Bi). The obtained ab-initio hybridization functions are taken as inputs to calculate the crystal-field splittings within NCA (non crossing approximation) and the tendencies are contrasted with experiments.

KEY WORDS: Highly correlated systems, crystal fields, p-electron.

CAC-CNEA, Av. Gral. Paz 1499, San Martín (1650), Buenos Aires, Argentina

rouira@tandar.cnea.gov.ar

Cerium monopnictides exhibit anomalous magnetic properties due to the magnetic anisotropy and to the particular hybridization strength of the 4f electron with the conduction band. The crystal-fields splittings ( $\Delta_{CF}$ ) of the 4f level in the heavier monopnictides (CeBi and CeSb) are considerably smaller than in the lighter Ce monopnictides (CeAs, CeP). This behaviour was previously studied and understood by Wills and Cooper [1]. The dominant contribution to the splittings in these monopnictides can be obtained from the point-charge (PC) model which is appropriate for insulators or ionic systems. This PC model alone can account for the CF splittings of Rare Earth monopnictides when the Rare Earth goes from Pr to Tb but it fails to describe Ce monopnictides because in Ce compounds the 4f-band hybridization cannot be neglected.

Wills and Cooper consider that the total  $\Delta_{CF}$  in these CeX systems is the result of two independent contributions with different sign: the extrapolated value from the PC model with non-hybridized 4f levels and the splittings induced by hybridization. The former gives rise to positive splittings which increase from Bi to P. In the cubic point group, the multiplet  $J = \frac{5}{2}$  decomposes into the  $|\frac{5}{2}; \Gamma_7\rangle$  doublet and the  $|\frac{5}{2}; \Gamma_8\rangle$  quartet. So that a positive splitting means that  $\Gamma_7$  is the ground state. They calculate the 4f hybridization function out of the conduction band density of states which is ob-

tained from first principles, using the linear muffin-tin-orbital (LMTO) method and the self-consistent potential within the atomic-sphere approximation (ASA) which does not contemplate the anisotropy of the crystalline environment. Within these calculations the 4f state is treated as a core state. Then, they calculate the hybridization contribution to  $\Delta_{CF}$  for CeX (X=P, As, Sb and Bi) on the basis of the Anderson Hamiltonian using second order perturbation theory. These hybridization contributions have an opposite sign to that of the PC model. In this way, they can explain the suppression of the crystal-field splitting of the heavier Ce monopnictides observed from the experimental data.

In the present work, we calculate  $\Delta_{CF}$  for this series of monopnictides in a different way. We perform *ab initio* calculations using the Full Potential-LAPW method within the local density approximation (LDA) [2] instead of the ASA potential and we treat the 4f states as part of the valence band. We then calculate the projected 4f-densities of states,  $\rho_{mm'}$ , for the systems at the experimental volumes (where  $m$  runs for the seven irreducible representations for a cubic environment) and compute the hybridization function,  $\Gamma_{mm'}(\epsilon)$ , following ref. [3, 4].

The different  $\Gamma_{mm'}(\epsilon)$  contain detailed information of the electronic structure of each system and are used as input for the Anderson Impurity model which is solved within an extended non-crossing approximation (NCA). In the Anderson model the value of the *bare*  $f$  energy level,  $\varepsilon_f$ , is taken as the experimental value that comes out of photoemission spectra [5]. This LDA-NCA approach has already been applied to cubic and tetragonal *Ce* based systems to calculate  $\Delta_{CF}$ 's and the trend in the

Kondo energy scales yielding results in good agreement with the available experimental information [4, 6].

Within this technique  $\Delta_{CF}$ 's arise from band-f hybridization and the anisotropy of the crystalline environment.

Experimental data of the CF splittings for the compounds under study in the present work are the following: 8 K for *CeBi*, 37 K for *CeSb*, 159 K for *CeAs* and 172 K for *CeP*. All the compounds have been reported to have the  $\Gamma_7$  multiplet as the ground state [7]. There is no available data for *CeN*.

Figure 1 and 2 show the calculated hybridization function for *CeP* and *CeSb*. In the inset, the detailed structure of these functions around the Fermi energy is shown and the  $\Gamma_7$  and  $\Gamma_8$  average values are explicitly shown. It can be observed that while the unoccupied states are governed by the  $\Gamma_8$  symmetry, close to the Fermi level the  $\Gamma_7$  one is stronger. As it is discussed in another contribution to this conference [8], the 5d-Ce band hybridizes mainly with the  $\Gamma_7$  4f states while the p-X band with the  $\Gamma_8$  4f states.

Whithin this model, a stronger  $\Gamma_8$  hybridization would imply a  $\Gamma_8$  symmetry for the ground state. If we consider the CF splittings that result from the LDA calculations taking into account the whole energy range for the conduction band (up to 1 Ry approx.), we obtain that the ground state is  $\Gamma_8$  for all the CeX series and a decreasing  $\Delta_{CF}$  from N to Bi, the value of the splittings being much larger than the experimental data. The reason why these results disagree both in sign and magnitud of  $\Delta_{CF}$  is that the calculated hybridization function for the p-X band ( $\Gamma_8$ ) is overestimated due to the

fact that the LDA calculation does not account for the strong ionic character of these mononictides compounds. Wills and Cooper also obtain a strong hybridization for the p-X band which is compensated by taking into account the CF shift from the ionic point charge model. In the present work we are able to reproduce the correct trend of  $\Delta_{CF}$ 's if we consider the energy spectrum of the bands up to an energy of the order of 6000 K above the Fermi level, discarding the unoccupied states above that energy. With this criterion, we obtain a  $\Gamma_7$  ground state for all the series and the calculated values for the CF splittings are: 160K for CeP, 150K for CeAs, 70K for CeSb and 50 K for CeBi. For CeN we also obtain a  $\Gamma_7$  ground state and a splitting greater than room temperature.

As it is discussed in Ref. [8] the more important contribution to the  $\Delta_{CF}$ 's in this series of compounds comes from the energy dependent hybridization function around the Fermi level ( $E_F$ ). Within this energy range,  $\Gamma_7$  hybridization is stronger and the difference between the  $\Gamma_7$  and  $\Gamma_8$  hybridization strength varies along the series because within the Full Potential-LDA calculation we take the 4f states as part of the valence band giving rise to different CF splittings. We claim that the main contribution to the hybridization around  $E_F$  comes from the 5d-4f interaction. In the systems where the 4f states are more localized (CeBi, CeSb) the 5d-4f hybridization is smaller and in turn, a smaller CF splitting is obtained. We consider that the p-4f hybridization should not be that strong for these ionic compounds.

In previous calculations [4, 6], it was not necessary to cut the energy spectrum because those compounds (the cubic  $CeM_3$  and the tetragonal  $CeM_2Si_2$ ) do not present

such a strong ionic character and LDA can give an appropriate description of the conduction bands.

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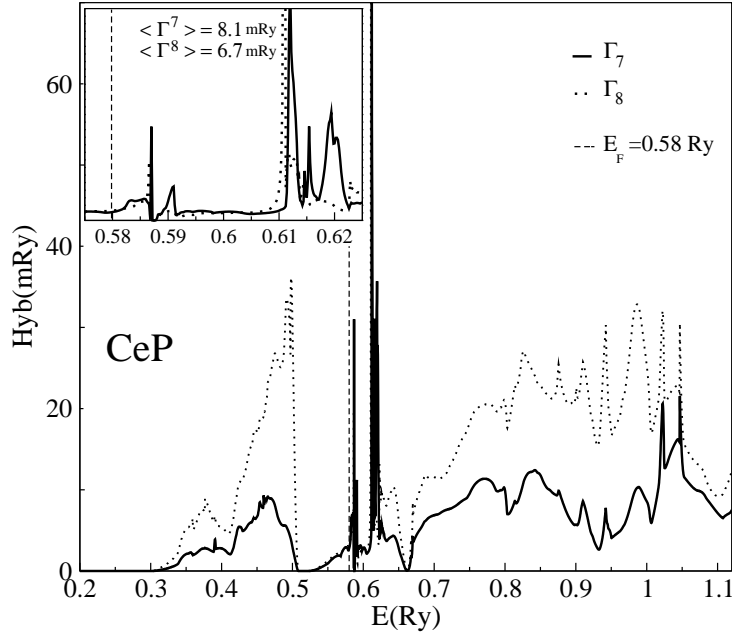


Figure 1: The calculated hybridization function for CeP between the conduction band and the  $\Gamma_7$  (solid curve) and  $\Gamma_8$  (dashed curve) 4f states. In the inset a detail of the hybridization around the Fermi level.

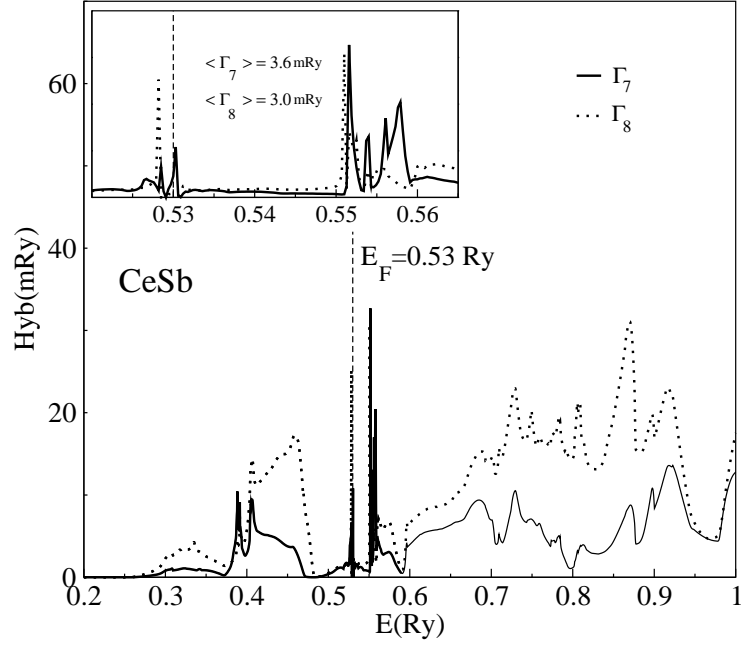


Figure 2: *Idem* than in Fig. 1 but for CeSb.